# An Investigation of the Supersolubility Relations of Seeded Solutions

By

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# AN INVESTIGATION OF THE SUPERSOLUBILITY RELATIONSHIPS OF SEEDED SOLUTIONS

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A Thesis

Presented to

the Graduate Faculty of

Lehigh University

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

---

by

William James Walsh

Lieutenant, U. S. Navy

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CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

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# CHAPTER I

## THE PROBLEM

Crystallization has been well recognized as a unit operation in the field of chemical engineering for many years. The industrial and economic importance of this unit operation is great. However, although much work has been done in the design of large commercial crystallizers, in the theoretical study of solution and melt chemistry, and in the technical aspects of giant crystal formation, very little is found in the literature on the basic aspects of crystal formation and growth in seeded solutions.

Statement of the problem It was the purpose of this study (1) to design and construct a reasonable apparatus for conducting batch crystallizations on a laboratory scale under controlled conditions; and (2) to show its feasibility for use in determining the supersolubility relationships of various salts in aqueous solutions.

Importance of the study It has been common practice in chemical engineering to consider crystal growth as simply the reverse process of solution of soluable material.[1] This

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[1] W. L. Badger, and W. L. McCabe, Elements of Chemical Engineering (New York: McGraw-Hill, 1936), p.240.

simplified concept plus the difficulties in constructing and operating the required apparatus to control all the variables entering into a crystallization process has served to keep this study within the realm of the pure scientist and, to a limited extent, the metallurgist. All this has resulted in chemical engineers using empirical methods to develop crystallizers which, although developed to a high degree of excellence for specific purposes, have lacked the theoretical basis necessary to give them general applicability. This work, in a small way, adds to the required basic knowledge.

Organization of the remainder of the thesis The work of this study naturally divided itself into two rather independent categories. The first was the design and construction of a suitable apparatus capable of allowing exact investigation of the effect of various crystallization variables such as cooling rate, agitator speed, etc. The second phase of the work consisted in using this apparatus to study some of the supersolubility relationships of ammonium sulfate. The remainder of this thesis will s ow the results of this work including in Chapter II a review of previous work; in Chapter III the procedure used for proving the capabilities of the apparatus for studying the supersolubility relationships of salts; in Chapter IV the results obtained and lastly in Chapter V a summary of the

results and the conclusions drawn.

## CHAPTER II

## REVIEW OF THE LITERATURE

The design and construction of constant temperature apparatus has received much attention in the literature but its use for the purpose of this work proved on investigation to be of slight value. Only one controlled cooling devise suitable for this work is known to have been previously constructed and a brief description of this is given. Similiarly, although much has been written in regard to the theoretical and fundamental aspects of the causes and types of crystal formation and growth, little is found on the more practical subject of crystal formation in seeded solutions. A summary, in the light of this work, of the basic knowledge and its extension to crystallization from seeded solutions is given.

Literature on cooling apparatus The design and construction of constant temperature baths has received wide attention in the literature.[1,2] However this work required

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[1] Findlay, Practical Physical Chemistry, (New York: Longmans, Green Co., 1925), P. 57.

[2] F. O. Schmidt and O. H. Schmidt "A Vacuum Tube Method of Temperature Control" Science, 73: 289, 1931.

not the relatively easily obtained constant temperature but rather it had the more difficult assignment of an apparatus, simple in design, which could cool a crystallizer of at least the size of a one liter beaker at a controlled rate with a precision better than 0.1 degrees Centigrade per minute. Further it must be able to allow variation in this controlled rate and to have this control over at least the range 25 to 65 degrees Centigrade. In addition ready access to the top of the crystallizer is required and the entire crystallizer must be visible at all times. The construction of such an apparatus has been reported.[3] This consisted of a one liter beaker used as a batch crystallizing unit inserted in a glass bell jar. The cooling medium was a mineral oil circulated through the bell jar from an external reservoir where the required control was obtained by means of a cooling coil and an electrical heater, although a small electrical heater was also used in the bell jar. This apparatus required the cooling medium to be heated to about 5 degrees Centigrade above the desired temperature before being added to the reservoir. It is reported that "...manual control proved to be satisfactory and the temperature of the solution could

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[3] H. H. Ting, and W. L. McCabe, "Supersaturation and Crystal Formation in Seeded Solutions", Industrial and Engineering Chemistry, 26: 1201, 1934.

easily be regulated within 0.05 degrees Centigrade."[4]

Literature on crystallization The study of the solid state and particularly substances of a crystalline nature, that is substances in which the constituent atoms or molecules are regularly arranged, has long been the object of study. According to Glasstone the study of crystals has two aspects, the examination of the external form and the elucidation of the internal structure.[5] Although the importance of both these studies cannot be overlooked, especially the latter which has been given great impetus and has produced an amazing amount of knowledge due to the development of the X-Ray method of study, neither aspect has produced suitable ideas on crystal formation which lead to the practical results required by this study.

This has not prevented the development of theories on crystal formation and growth. Buckley[6] in his most complete book reviews the many current ideas such as the Curie theory of growth, the many diffusion theories, the absorption layer theory and all their many modifications

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[4] Ibid., p. 1203

[5] S. Glasstone, Textbook of Physical Chemistry (New York: Van Nostrand Co. 1946), p. 340.

[6] H. E. Buckley, Crystal Growth (New York: Wiley, 1951). chap. 3, 5, 6.

easily be regulated within 0.02 degrees centigrade.[4]

Literature on crystallization. The study of the solid state and particularly substances of a crystalline nature, that is substances in which the constituent atoms or molecules are regularly arranged, has long been the object of study. According to Glasstone the study of crystals has two aspects, the examination of the external form and the elucidation of the internal structure.[5] Although the importance of both these fields cannot be overlooked, especially the latter which has been live coal i years and has produced an amazing amount of knowledge due to the development of the X-ray method of study, neither aspect has produces sufficient ideas on crystal formation which lead to the practical results required by this study.

This has not prevented the development of theories on crystal formation and growth. Volmer[6] in his most complete book reviews the many current ideas such as the cubic theory of growth, the surface diffusion theories, the adsorption layer theory and his single layer modifications

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[4] Ibid., p. 120.

[5] S. Glasstone, Textbook of Physical Chemistry, (New York: Van Nostrand Co. Inc., 1940), p. 1.

[6] M. Volmer, Kinetik der Phasenbildung (Dresden: Steinkopff, 1939), p. 1.

by various workers. The sad fact is that although each of these theories has some experimental basis none has been conclusively shown to be valid.

With theoretical studies thus giving no practical information at this time, one must consider the behavior of solutions during crystallization if one is to gain guidance of the type desired in this work. Here one is inevitably led to the studies of solubility and supersolubility of Miers and his followers. Essentially their work involved the use of changes in refractive index of solutions to locate the "metastable" and "labile" fields lying on the supersaturated side of the solubility curve. Their work involved a great variety of solutions with the following general conclusions quoted from Buckley on page 9, using Figure 1 of this work:

> A represents a point in the region of unsaturation which, if undisturbed, would remain as a single phase indefinitely. A crystal placed in such a solution would dissolve. There are two ways in which we can bring a solution represented by the temperature and concentration of A to the equilibrium "saturation" condition. First, by lowering the temperature to the point B or, second, by evaporating off some of the water at constant temperature, when the conditions of the point B' will be reached. In many cases of crystallization in the laboratory, neither of these processes is strictly carried out, as evaporation may be allowed at the same time as the temperature is lowered. With either solution, at B or B', a crystal would remain indefinitely without growth or dissolution taking place. Theoretically any further cooling below point B or withdrawal of solvent beyond point B' ought to result in the separation of solid(i.e. crystallization), but it is a matter of

common experience that this never occurs, though growth will take place on crystals already there. Further cooling will bring us to the point C, where the slightest shock or disturbance will bring about immediate crystallization. The moment this occurs, the heat of solidification will prevent any further substantial drop in temperature until the crystals have gathered to themselves most of the available excess represented by the distance from the equilibrium curve.

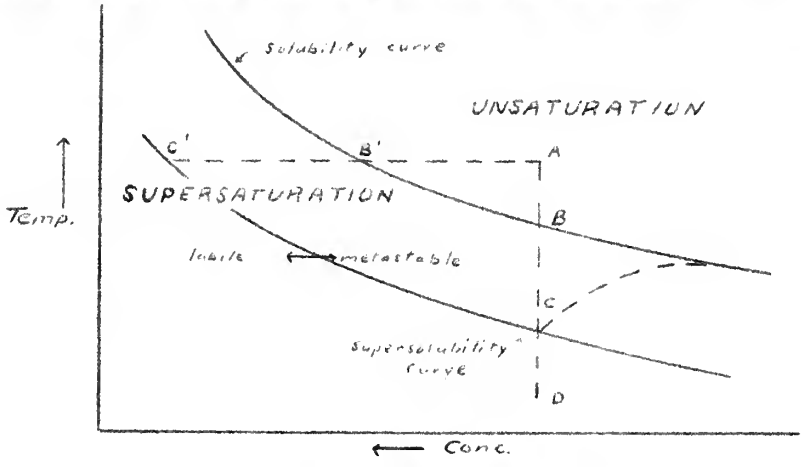


Figure 1

DIVISION OF THE SOLUBILITY

FIELD ACCORDING TO MIERS

Serious objections to these conclusions exist, attacking the idea of a metastable field. Young showed that by the application of mechanical stimulation to a supersaturated solution in the metastable region crystallization could be caused to occur without seeds. He concluded, " ...it seems no longer necessary or even justifiable to assume the existence of a metastable limit in the generally accepted sense....The whole unstable field is labile and

common experience that this never occurs, though growth will take place on crystals already there. Further cooling will bring us to the point $c_1$ where the all-most smooth distribution will begin about immediate crystallization. The moment this occurs, the most of solidification will prevent any further substantial drop in temperature until the crystals have gathered to themselves most of the available excess represented by the distance from the equilibrium curve.

Figure 1

DIVISION OF THE MATERIALITY

[illegible]

Various objections to these considerations exist, according the idea of a materiable field. Some showed that by the application of conceptual eliminations to a sufficient number solutions in the materiable [illegible] crystallization could be caused to occur without [illegible]. [illegible] noted, " ...It seems to be necessary [illegible] even justifiable to assume the existence of a materiable field in the generally accepted sense.... [illegible] be filled in [illegible] and

crystallization may be brought about in any portion of it by the production of sufficient mechanical shocks."[7]

Ting and McCabe[8] followed up the attack on the metastable field by showing that if a seeded solution of magnesium sulfate heptahydrate of a definite concentration is cooled at a definite rate, in the presence of seeds of a definite size and number added at the temperature where the solution became just saturated, the moment of formation of the new crystals is fixed and reproducible but that the amount of supersolubility varied with all these factors. They further showed that another reproducible point for the salt in question was obtained where the rate of formation of new nuclei was a maximum.

McCabe in the section on Crystallization in Perry[9] after noting the reproducibility mentioned above states

> ...whereas the supersaturation curves of the Miers type are difficult to reproduce except under carefully controlled conditions, as it is difficult to prevent the effects of fortuitous seeding. The supersaturations obtained in seeded solutions are definitely considerably less than those found in crystallizing unseeded solutions.

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[7] S. W. Young "Mechanical Stimulus to Crystallization in Supercooled Liquids", Journal of the American Chemical Society, 33: 159, (1911)

[8] Ting and McCabe, op. cit., p. 1205.

[9] J. H. Perry, editor, Chemical Engineers' Handbook, (New York: McGraw-Hill, 1950), p. 1054.

These results indicate that the ability of crystals to inoculate a solution and to cause the formation of new crystals is an important fundamental factor in crystallization.

Since in any crystallization process the nuclei formation must be under control if the crystal growth and the size distribution in the resulting crop is to be under control the work of Ting and McCabe showed promise of giving valuable information in this direction, and thus the scope of this work was directed along those lines and the following pages give the procedure, results and conclusions.

# CHAPTER III

## EXPERIMENTAL PROCEDURE

Building the crystallizer The major work to be reported in this thesis involves the design and assembly of the apparatus. As stated above the requirements were neither few nor compatable. Minimum requirements were:

1 A reasonable simple piece of equipment.

2 Control of the cooling rate within 0.05 degrees Centigrade up to a rate of 2.00 degrees Centigrade per minute.

3 Knowledge of the temperature of the solution at any time to 0.05 degrees Centigrade.

4 Control of the crystallizer agitator within 10 revolutions per minute.

5 Easy access to the solution being crystallized for such purposes as adding seeds, removing samples, etc.

6 Easy installation and removal of the crystallizer itself.

7 Elimination of all appreciable effects of ambient conditions.

8 Entire contents of crystallizer clearly visible at all times.

9 A bath temperature of 70 degrees Centigrade, attainable within a reasonable time.

# CHAPTER III

## A MATHEMATICAL PROBLEM

Making the crystallizer. The major work to be reported in this thesis involves the design and assembly of the apparatus. As before stated the requirements were neither few nor contradictory. Primary requirements were:

1. A reasonable simple piece of equipment.
2. Control of the cooling rate which may be required continuous up to a rate of 4.0) degrees centigrade per minute.
3. Provision of the necessary of the solution as may be due to 0.01 in pure ethyl acetate.
4. Control of the crystallizer against which in rotary fashion for stirrer.
5. Easy access to [illegible] and [illegible] [illegible] [illegible] etc.
6. [illegible] in [illegible] crystallizer [illegible] [illegible]

Although Tings apparatus[1] did fulfill most of these requirements it was felt that it seriously violated the first requirement, for it was far from a simple piece of equipment. It was decided to attempt all control within the bath itself, thus eliminating all of Tings external heating plus auxiliary reservoir. A large, cylindrical pyrex glass jar 10 inches in diameter and 18 inches deep was obtained. Preliminary runs with this as the cooling bath for a solution contained in a one liter beaker showed possibilities of giving the required control.

To eliminate the effects of the surroundings this glass jar was placed in a cardboard container 18 inches in diameter and the intervening space was filled with rock wool lagging after two ports had been constructed by cutting holes in the cardboard and lining the ports with sheet metal and closing them with transparent plastic to provide the insulating effect of a dead air space.

For positive control of the cooling rate there was installed in the bath a 600 watt electrical resistance heater and a cooling coil of 1/8 inch copper tubing which was connected to the laboratory water supply. Control

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[1] Ting and McCabe, op. cit., p. 1201

was obtained by use of a powerstat connected to the heater and by means of a needle valve, orifice and manometer in the discharge line of the cooling coil. Careful and experienced manipulation gave the control required.

The crystallizer itself was a one liter beaker, with three aluminum baffles 3/16th of an inch wide. The crystallizer impeller was made of acrylic plastic mounted on the shaft of a 1/4 HP motor, the speed of which was controlled within the desired range by connecting to a powerstat.

Three cover plates of three eights inch plywood were designed and made. One was for the insulating jacket. Another was a cover for the bath with openings for heating coil, cooling coil, bath stirrer and crystallizer. The crystallizer was supported in the bath by the bath cover in such a position as to be readily visible through one port in the insulating jacket while illuminated by a beam of light entering through the other port. After the crystallizer was in place the third cover plate, was placed on it and bolted to the jacket cover. This crystallizer cover had openings for the crystallizer stirrer, crystallizer thermometer and an opening for seed input, sampling of solution, etc.

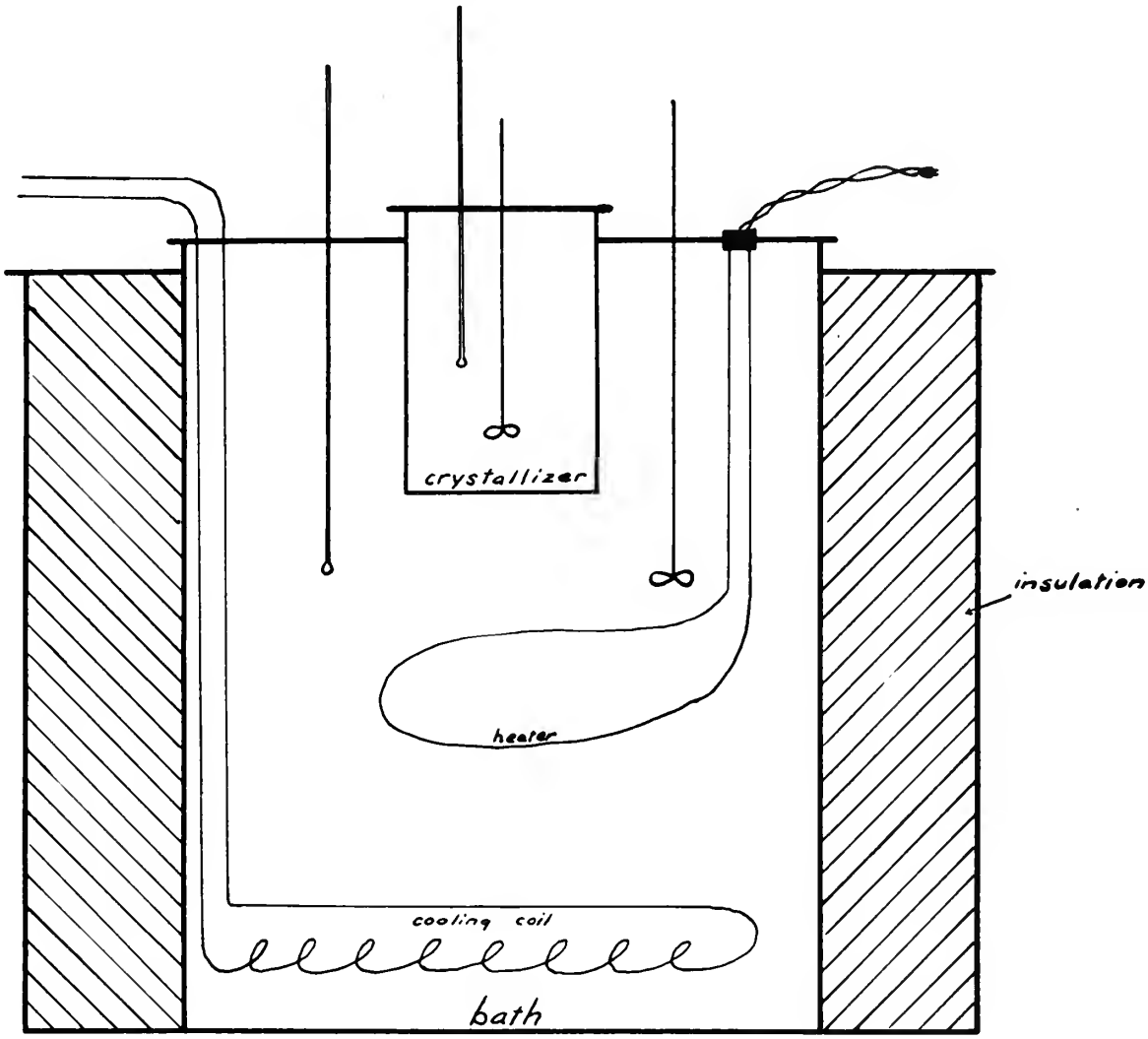
The crystallizer thermometer could be read to 0.01 degrees Centigrade. Other equipment included a bath thermometer and thermometers reading inlet and outlet temp-

eratures of the cooling water and a bath stirrer. All thermometers other than the crystallizer thermometer read to 0.1 degree Centigrade. A sketch of the complete assembly is shown in Figure 5.

By adjusting the powerstat and flow of cooling water the desired rate of cooling was obtained. This was most satisfying for all through the long period of design and assembly no assurance was had that this would be the case.

Preparation of solutions After trying several methods it was found most convenient and accurate to prepare the solutions directly in the crystallizer. A dry beaker was first tared and then a given weight of C.P. ammonium sulfate was added. To the beaker was then added the necessary weight of distilled water to bring the final solution to the required concentration. The crystallizer was then placed in position in the bath, which had been raised to 10 to 15 degrees above the saturation temperature of the solution, the crystallizer stirrer was started and the run was not commenced until the solid phase was completely dissolved.

Preparation of seeded crystals The seed crystals were prepared by screening C.P. ammonium sulfate using Standard U. S. Mesh testing sieves. The cut -40 +50




| | | |
|---|---|---|
| CHEMICAL ENGINEERING DIVISION<br>LEHIGH UNIVERSITY<br>BETHLEHEM, PA. | FIGURE 2<br>ASSEMBLY OF<br>APPARATUS | DRAWN BY W. WALSH<br>DATE 15 AUGUST 1951<br>NO. |

was used for the runs reported in this paper.

Procedure for making a run When the salt was completely dissolved as described above, the powerstat and cooling water flow was set to give the desired cooling rate. Such manual adjustment of course required continual resetting and doing this at five minute intervals proved satisfactory. The speed of both the crystallizer and bath stirrers was set to the desired rpm and when the rate of cooling was under control the following data were taken every five minutes:

crystallizer temperature
crystallizer stirrer speed
crystallizer stirrer motor powerstat setting
bath heater powerstat setting
temperature of inlet and outlet cooling water
cooling water manometer setting
bath temperature

During the run seed crystals of the desired size were weighed out. The seeds were introduced into the crystallizer when the solution reached the saturation temperature, and the time and temperature were noted.

After the seeds were introduced the crystallizer was carefully watched to determine that (a) no seeds dissolved, (b) the seeds grew as expected and (c) the point of maximum formation of nuclei was discernible. Doing this and at the same time taking readings and adjusting the cooling rate controls really required the help of an assistant

was used for the runs reported in this paper.

Procedure for making a run. When the melt was completely dissolved as described above, the powerstat and cooling water flow was set to give the desired cooling rate. Such manual adjustment of course required continual resetting and doing this at five minute intervals proved satisfactory. The speed of both the crystallizer and bath stirrers was set to the desired rpm and when the rate of cooling was under control the following data were taken every five minutes:

crystallizer temperature
crystallizer stirrer speed
crystallizer stirrer motor current setting
bath heater powerstat setting
temperature of inlet and outlet cooling water
cooling water manometer setting
bath temperature

During the run some crystals of the desired size were weighed out. The seeds were introduced into the crystallizer when the solution reached the saturation temperature, [illegible] the [illegible] were weighed.

After the seeds were introduced the crystallizer was carefully [illegible] the (a) [illegible] (b) [illegible] (c) [illegible] [illegible] [illegible]

although none was available.

After the run was completed the crystallizer was removed from the bath, wiped dry and weighed to determine the loss by evaporation.

Typical data sheet The data taken during Run No. 6 are shown in Table I.

TABLE I

TYPICAL DATA SHEET

FOR RUN 6

Run 6 - 40° C. = 486.0 $\frac{9(NH_8)_2SO_4}{600_9\ H_2O}$

7/23/51

| | | | |
|---|---|---|---|
| Wt. beaker | 285.7 | Seeds | |
| Wt. Salt | 486.0 | 0.2g. | (-40 +50) |
| Wt. Total | 771.7 | | |
| Wt. $H_2O$ | 600.0 | $T_{amb}$ | 26.8 |
| Wt. Total | 1371.7 | | |

| Time | $T_{cryst}$ | $T_{bath}$ | Heater Rheo. | Cryst. Rheo. | Cryst. RPM | Man. Set | Cooling Coil $T_{in}$ | Cooling Coil $T_{out}$ |
|---|---|---|---|---|---|---|---|---|
| 5:45 | 52.50 | 52.1 | 110 | 38 | 130 | 1 | 47.6 | 18.8 |
| 50 | 51.90 | 51.0 | 110 | 38 | 126 | 1 | 47.0 | 18.8 |
| 55 | 49.48 | 49.5 | 100 | 38 | 130 | 1 | 46.8 | 18.8 |
| 6:00 | 48.09 | 48.1 | 90 | 38 | 130 | 1 | 45.6 | 18.8 |
| 05 | 46.68 | 46.4 | 90 | 38 | | 1 | 44.0 | |
| 10 | 45.34 | 45.2 | 90 | 38 | 130 | 1 | 43.0 | 18.8 |
| 15 | 44.13 | 44.2 | 90 | 38 | | 1 | 42.0 | |
| 20 | 42.98 | 43.1 | 85 | 38 | | 1 | 41.4 | |
| 25 | 41.80 | 42.0 | 75 | 38 | 126 | 1 | 39.8 | 18.8 |
| 30 | 40.77 | 40.8 | 65 | 38 | | 1 | 38.8 | |
| 35 | 39.46 | 39.5 | 55 | 38 | | 1 | 37.6 | |
| 40 | 38.29 | 38.1 | 50 | 38 | 128 | 1 | 36.5 | 18.8 |
| 45 | 37.20 | 37.0 | 40 | 38 | | 1 | 35.7 | |
| 50 | 36.10 | 36.0 | 25 | 38 | | 1 | 34.7 | |
| 55 | 35.02 | 35.0 | 10 | 38 | 130 | 1 | 33.6 | 18.8 |
| 7:00 | 33.85 | 33.8 | off | 38 | | 1.5 | 32.0 | |
| 05 | 32.51 | 32.0 | off | 38 | | 2.0 | 30.8 | |
| 10 | 31.30 | 31.0 | off | 38 | 130 | 2.2 | 29.4 | 18.8 |
| 15 | 30.11 | 30.0 | off | 38 | | 2.5 | 28.2 | |
| 20 | 28.50 | 28.3 | off | 38 | 130 | 3.0 | 27.1 | 18.8 |

# TABLE I

## TYPICAL DATA SHEET

## FOR RUN 6

Run 6 - 40° C. = 486.0 $\frac{(\text{MHg})\,2.304}{600\text{g } H_2O}$

7/23/51

| | | | |
|---|---|---|---|
| Wt. Beaker | 285.7 | Seeds | |
| Wt. Salt | 486.0 | 0.25g.(-40 +50) | |
| Wt. Total | 771.7 | | |
| Wt. $H_2O$ | 600.0 | $T_{amb}$ | 21.8 |
| Wt. Total | 1371.7 | | |

Cooling Coil

| Time | $T_{crystl}$ | $T_{bath}$ | Heater Rheo. | Cryst. Rheo. | Cryst. RPM | Man. Set | $T_{in}$ | $T_{out}$ |
|---|---|---|---|---|---|---|---|---|
| 5:45 | 52.50 | 52.1 | 110 | 30 | 130 | 1 | 47.6 | 18.8 |
| 50 | 51.90 | 51.0 | 110 | 30 | 126 | 1 | 47.0 | 18.8 |
| 55 | 49.45 | 49.5 | 100 | 38 | 130 | 1 | 46.8 | 18.8 |
| 6:00 | 46.09 | 46.1 | 90 | 38 | 130 | 1 | 45.6 | 18.8 |
| 05 | 46.66 | 46.4 | 90 | 38 | | 1 | 44.0 | |
| 10 | 45.34 | 45.2 | 90 | 30 | 130 | 1 | 43.0 | 18.8 |
| 15 | 44.13 | 44.2 | 70 | 38 | | 1 | 42.0 | |
| 20 | 42.98 | 43.1 | 85 | 30 | | 1 | 41.4 | |
| 25 | 41.00 | 42.0 | 75 | 30 | 126 | 1 | 39.0 | 18.8 |
| 30 | 40.27 | 40.0 | 65 | 30 | | 1 | 38.0 | |
| 35 | 37.46 | 37.7 | 75 | 30 | | 1 | 37.6 | |
| 40 | 36.29 | 35.1 | 80 | 30 | 120 | 1 | 36.2 | 18.8 |
| 45 | 37.20 | 37.0 | 70 | 30 | | 1 | 37.7 | |
| 50 | 37.10 | 36.0 | 80 | 30 | | 1 | 37.7 | |
| 55 | 37.02 | 37.0 | 10 | 30 | 130 | 1 | 37.7 | 18.8 |
| 7:00 | 33.05 | 33.0 | 075 | 30 | | 1.5 | 36.0 | |
| 05 | 32.51 | 32.0 | 075 | 30 | | 2.0 | 36.0 | |
| 10 | 31.30 | 31.0 | 075 | 30 | 130 | 2.2 | 29.4 | 18.8 |
| 15 | 30.11 | 30.0 | 075 | 30 | | 2.2 | 28.1 | |
| 20 | 28.30 | 28.0 | 075 | 30 | 130 | 3.0 | 27.1 | 18.8 |

# CHAPTER IV

## RESULTS

In the main series of experiments seven runs were made. All were satisfactory and are summarized below as well as on Table II, page 21, and on Curves 1, 2, 3, and 4 on pages 22 to 25.

Runs 1, 2, 3 These runs were preliminary in the sense that the technique of preparing the solutions and introducing the seeds had not been worked out. However control of the cooling rate was very easy at all times. Even Run 1 which was carried out over a three and one half hour period from 58.56 to 27.78 degrees Centigrade was controlled within 0.04 degrees Centigrade per minute. All succeeding runs were carried out at one rate.

Run 4 This was a successful run from the cooling rate standpoint but when the seeds (-40 +50 U. S. Standard Mesh) were introduced new crystals appeared to form at once.

Run 5 This was a one hour and fifty minute run from 51.50 to 24.90 degrees Centigrade of a solution with a saturation temperature of 40 degrees Centigrade. The cooling rate was 0.25 degrees Centigrade per minute and 0.5 grams

# CHAPTER IV

## RESULTS

In the main series of experiments seven runs were made. All were satisfactory and are summarized below as well as on Table II, page 21, and on Curves 1, 2, 3, and 4 on pages 22 to 25.

Runs 1, 2, 3 These runs were preliminary in the sense that the technique of preparing the solutions and introducing the seeds had not been worked out. However control of the cooling rate was very easy at all times. Even Run 1 which was carried out over a three and one half hour period from 48.56 to 27.70 degrees Centigrade was controlled within 0.04 degrees Centigrade per minute. All succeeding runs were carried out at one rate.

Run 4 This was a successful run from the cooling rate standpoint but when the seeds (-40 +50 U. S. Standard Mesh) were introduced new crystals appeared to form at once.

Run 5 This was a one hour and fifty minute run from 41.50 to 24.70 degrees Centigrade of a solution with a saturation temperature of 40 degrees Centigrade. The cooling rate was 0.20 degrees Centigrade per minute. [illegible]

of seeds (-40 +50) was used. Although the seeds grew as expected, and although nuclei were observed in the solution at the end of the run, the point of maximum rate of formation of new nuclei was never observed.

Run 6 This run was from 48.09 to 30.11 degrees Centigrade, saturation temperature 40.00 degrees Centigrade, cooling rate 0.25 degrees Centigrade per minute with the maximum rate over a five minute period being 0.28 and the minimum 0.21 degrees Centigrade per minute. Again as in Run 5 the seeds, 0.2 grams, grew in size, and nuclei did form but when their rate of formation became a maximum could not be determined.

Run 7 This was an unseeded run of a solution with a saturation temperature of 40.00 degrees Centigrade from 43.24 to 28.95 degrees Centigrade at the rate of 0.25 degrees Centigrade per minute. By stopping the crystallizer periodically after the saturation temperature was reached nuclei were detected at 34.42 degrees Centigrade. At 33.04 degrees transparent crystals were seen in the solution without stopping the stirrer. By the time 32.20 was reached many large white crystals were present. At 29 degrees the solution was full of crystals of all sizes.

of scale (~40 +40) was used. Although the scale was not as expected, and although nodal were observed in the soil plan at the end of the run, the point of maximum rate of deformation of new nodes was never observed.

Run 6 This run was from 40.09 to 30.11 degrees Centigrade, saturation temperature 40.00 degrees Centigrade, cooling rate 0.29 degrees Centigrade per minute with the maximum rate over a five minute period being 0.26 and the minimum 0.21 degrees Centigrade per minute. Again as in Run 5 two nodes, 1.2 inches, were in size, and nodal did form but when their rate of formation became a maximum could not be determined.

Run 7 This was an unsuccessful run of a solution with a saturation temperature of 1.0 degree Centigrade from 3.39 to 2.0 degrees Centigrade at the rate of 0.21 degrees per minute. Due to a leak in the refrigerator [illegible] the saturation temperature was reached [illegible] nodal were observed at 2.0 degrees Centigrade. At 1.0 degrees [illegible] [illegible] [illegible]

TABLE II

EXPERIMENTAL DATA ON

AMMONIUM SULFATE SOLUTIONS

| Run No. | Sat. Temp. °C. | Seed Crystals gm. | Stirrer Speed | Cooling Rate °C/min. | Action of Soln after seeds added |
|---|---|---|---|---|---|
| 4 | 40 | 1.0 | 200 | 0.40 | Crystals formed at once. |
| 5 | 40 | 0.5 | 200 | 0.25 | Seeds grew. Max. rate of formation of nuclei not discernible |
| 6 | 40 | 0.2 | 130 | 0.25 | Same as five |
| 7 | 40 | none | 200* | 0.25 | Nuclei observed at 34.42 by stopping stirrer periodically. No max. rate of formation discernible |

* The same impeller was used for Runs 4, 5, and 6. For Run 7 an impeller 1/6th of its size was used.

# TABLE II

## ADDITIONAL DATA ON

## AMMONIUM SULFATE AUTOCLAVES

| Run No. | Sat. Temp. °C. | Seed Crystals gm. | Stirrer Speed | Cooling Rate °C/min. | Action of Soln after seeds added |
|---|---|---|---|---|---|
| 4 | 40 | 1.0 | 200 | 0.40 | Crystals formed at once. |
| 5 | 40 | 0.5 | 100 | 0.25 | Seeds grew. Max. rate of formation of nuclei not discernible. |
| 6 | 40 | 0.5 | 120 | 0.25 | Same as five |
| 7 | 40 | none | 200* | 0.25 | Nuclei observed at 34.2 °C stopping stirrer periodically. No max. rate of formation discernible |

* The same impeller was used for runs 4, 5, and 6, but for run 7 an impeller 1/8th of its size was used.

FIGURE 3

Cooling Curve, Run 4

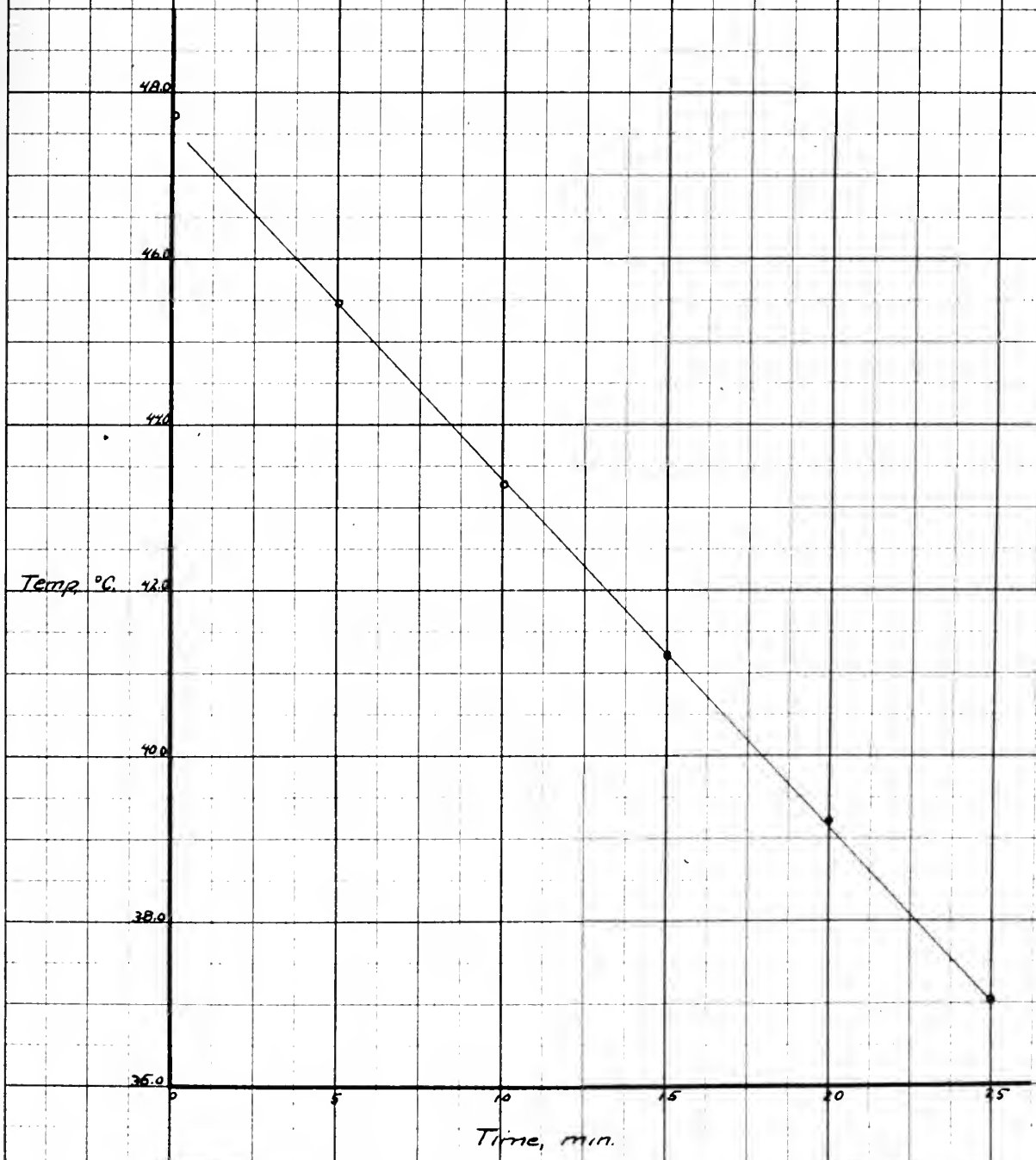


FIGURE 4

Cooling Curve. Run 5

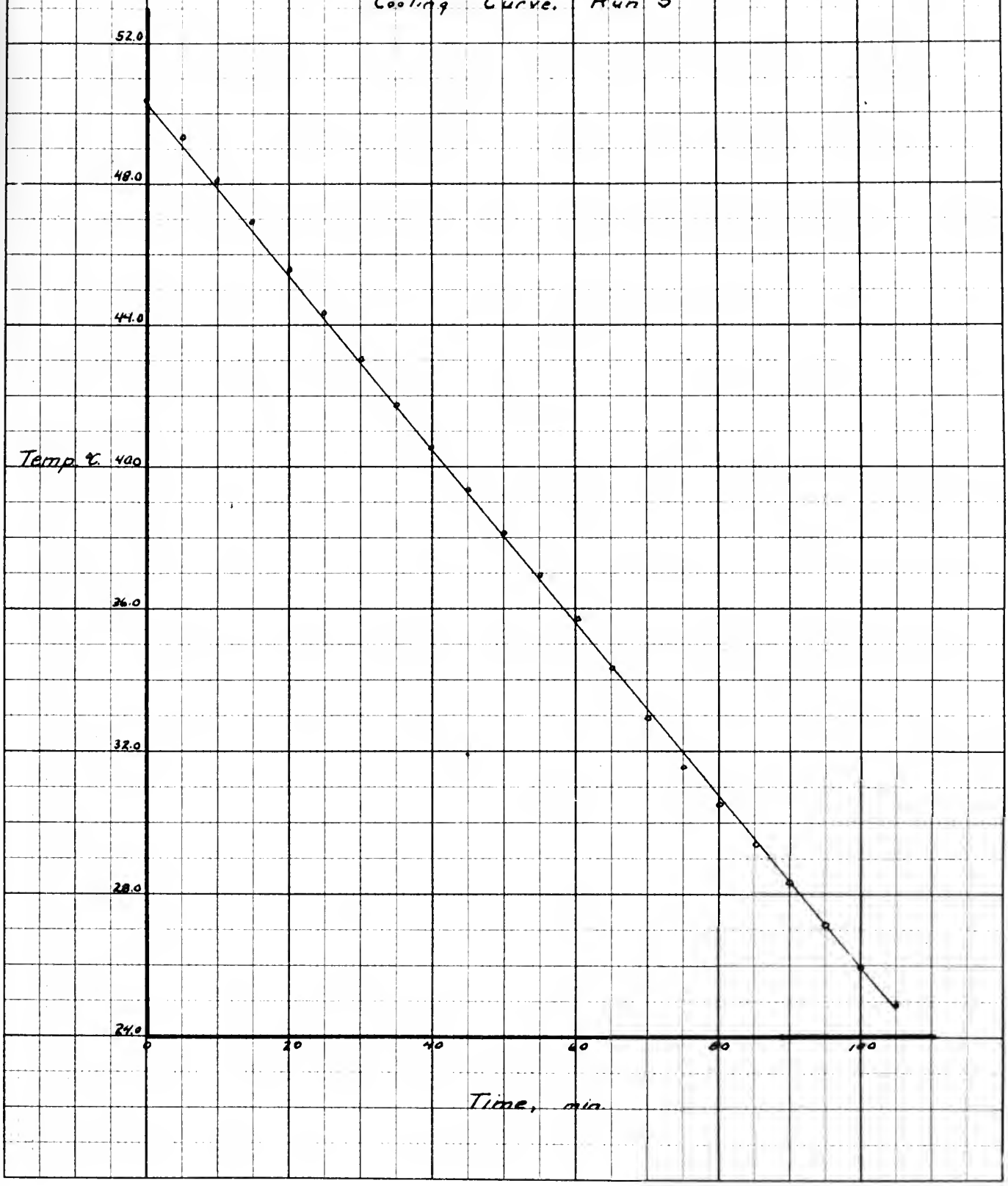


FIGURE 5

Cooling Curve. Run 6

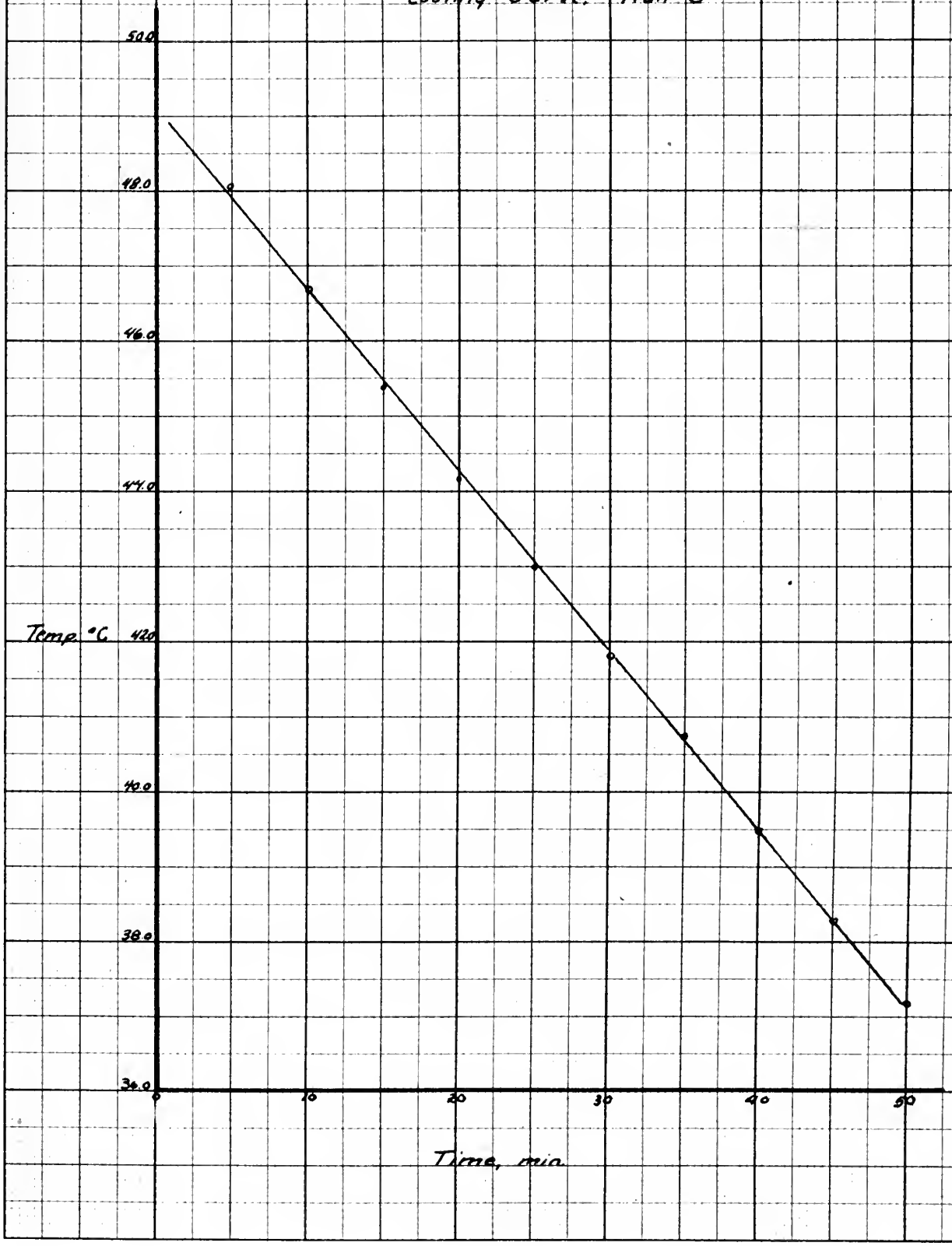
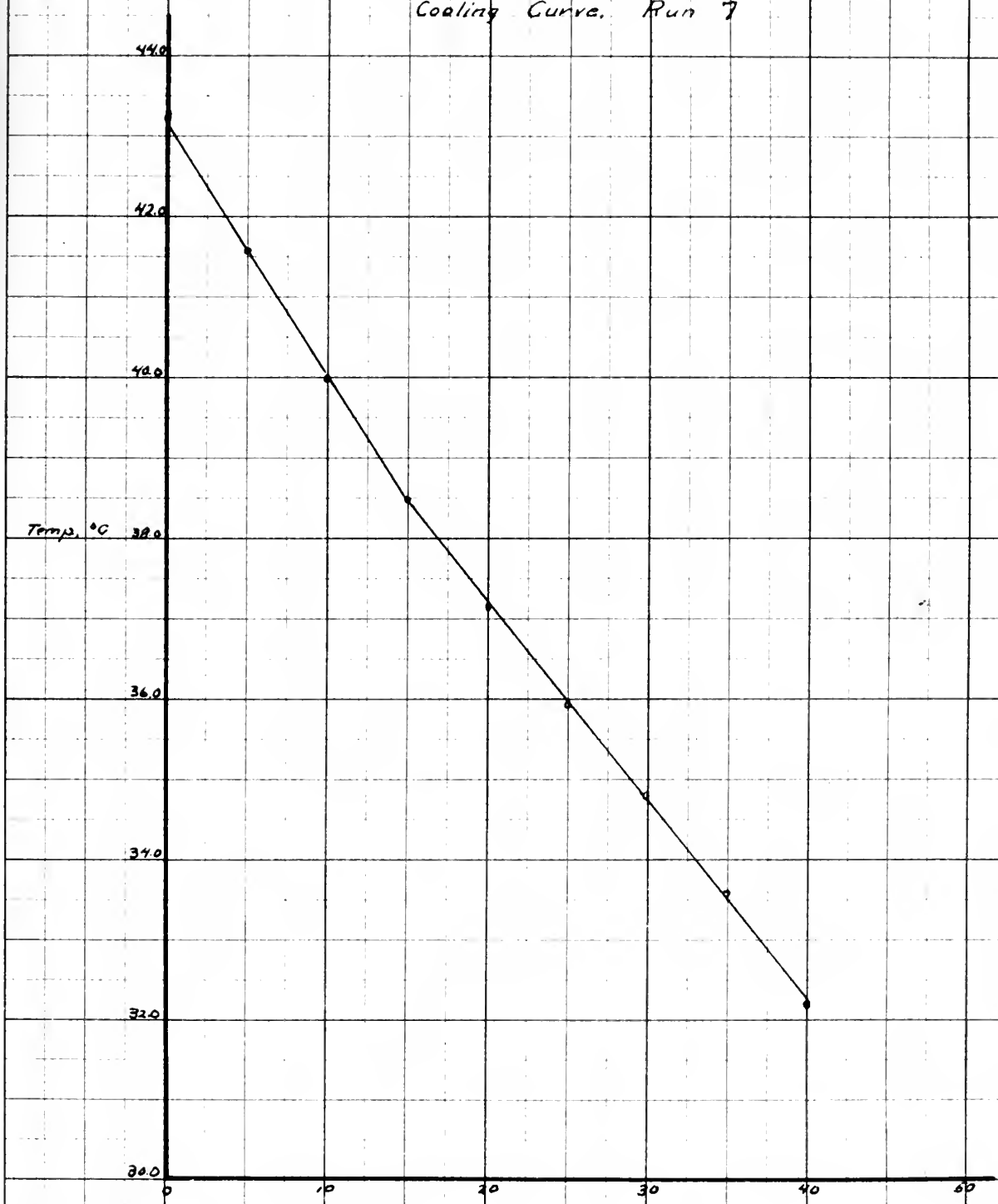


FIGURE 6

Cooling Curve, Run 7



# CHAPTER V

## SUMMARY AND CONCLUSION

Summary The attainment of the required control of heat loss was most gratifying and, it is felt, fulfilled the requirements of the first purpose of this work. However the failure to observe the point of maximum formation of nuclei was disappointing. Although the solution was carefully watched during a series of four runs, one of which was unseeded, no demarcation point was discernible. To be sure that the amount of seeds was not masking this point only 0.2 grams were used in Run 6 and no seeds were used in Run 7. Further an impeller of much smaller area, rotating at a low speed was used in Run 7, but to no avail.

The progress of the crystallization proceeded as follows: (1) the cooling rate was under control before the saturation temperature was reached; (2) at the saturation temperature the required amount of seeds was added; (3) the seeds were visibly observed to grow as the solution was cooled; (4) at some point during this period new nuclei formed, for one finally became aware of the fact that the number of crystals present had increased; (5) from that time the crystallizer became more and more full of crystals although at no time did one notice a "...copious evolution of

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nuclei."[1] Although nuclei certainly did form neither the moment of first formation not the time when formation became a maximum was visible.

These results demand a more critical analysis of the work of Ting and McCabe. The first consideration is that this is the only work that has been reported in the field of seeded solutions and it considered only magnesium sulfate heptahydrate although McCabe has stated[2] "...supersaturated solutions of KCl show the same type of behaviour." It is felt significant (1) that although the original work was done prior to June 1934, no additional work has been published along the same lines and (2) that the salt chosen, magnesium sulfate heptahydrate, was a rather unusual choice for work in the field of chemical engineering since many other salts are of greater practical importance. It was for this latter reason that ammonium sulfate was chosen for this work.

One is thus lead to the conclusion that the choice of magnesium sulfate heptahydrate was most fortuitous, or was one carefully made after preliminary work, not reported, which showed that this salt would give the desired results in a discernible and reproducible way.

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[1] Ting and McCabe, op. cit., p. 1206.

[2] Perry, op. cit., p. 1055.

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These results demand a more critical analysis of the work of Ting and Wadde. The first consideration is that this is the only work that has been reported in the field of seeded solutions and it considered only an aqueous sulfate monohydrate although iodine was added[2] "...supersaturated solutions of KCl show the same type of behavior." It is fair significant (1) that although the original work was done prior to June 1934, no additional work has been published along the same lines and (2) that the salt chosen, magnesium sulfate monohydrate, was a rather unusual choice for work in the field of chemical crystallization since only other salts are of major commercial importance. It was for this latter reason that ammonium sulfate was chosen for this work.

One is also left to wonder why the problem of supersaturation seldom, otherwise and most interesting, or was one generally seen since preliminary work, not reported, which showed that, in salt solutions, the 3 Angstrom region is a likely and reasonable one.

---

[1] Ting and Wadde, J. Phys. Chem., 38, 1.

[2] Ting, J. Phys. Chem., 38, 1.

McCabe has reported[3] that a solution of magnesium sulfate heptahydrate will support supercooling of about 17 degrees C. without nucleus formation while for sodium chloride supersaturation is negligible. Thus at least qualitative information is had for four salts, magnesium sulfate heptahydrate, potassium chloride, sodium chloride, and ammonium sulfate. Of these, two give definite, reproducible points of undercooling where nuclei form and where their rate of formation becomes a maximum while the other two do not give any outward appearance of such abrupt changes.

Investigation as to the reason for this difference in outward behaviour leads one to investigate solubility data. The solubility of each of these salts in water at 30 degrees C. is as follows:[4]

| | |
|---|---|
| Ammonium sulfate . . . . . | 78.0g./100g.$H_2O$ |
| Magnesium sulfate heptahydrate . . . | 40.8 |
| Potassium chloride . . . . . | 37.0 |
| Sodium chloride . . . . . | 36.3 |

It is thus seen that salts with the highest and lowest solubilities exhibit similar tendencies.

Other lines of thought produce similar inconclusive

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[3] Badger and McCabe, op. cit., p. 442

[4] Perry, op. cit., Table 140, p. 196

results and one is lead to agree with McCabe "... stirring rate, average distance between crystals, total surface available on existing crystals and purity of the solution. The action of all of these factors is greatly modified by the nature of the solute. At present no quantitative treatment of these factors is possible."[5]

Before leaving this discussion which so intimately involves Tings work a further criticism must be made of the manner in which he detected the initial formation of nuclei. To quote from his work, "The first spontaneous appearance of crystals could be detected by stopping the stirrer temporarily to let the seed crystals settle and observing what happened .... After the seed crystals had been added stirring was stopped frequently to locate the temperature at which new crystals first appeared."[6] It is felt that no reasonable conclusions can be drawn of the effect of stirrer speed on the amount of undercooling which a solution can support using this method. All previous work has shown the sensitiviness of supercooled solutions to external conditions and it is reasonable to expect that the frequency and interval of stopping as well as the time of acceleration and deceleration of the stirrer will have an effect.

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[5] Badger and McCabe, op. cit., p. 444.

[6] Ting and McCabe, op. cit., p. 1204

<u>Conclusions</u> The following conclusions are drawn from this work:

1 An apparatus to give controlled cooling of a solution container in a one liter beaker can be constructed without extensive or expensive equipment.

2 Such an apparatus can be expected to have control of the cooling rate within 0.05 degrees Centigrade.

3 If such an apparatus is used for crystallization investigations of the type described in this work, two operators are required for at least part of the run if precise runs are to be confidently expected.

4 Ammonium sulfate does not exhibit definite, reproducible temperatures where a supersaturated solution first forms nuclei, nor where the rate of formation of new nuclei becomes a maximum.

5 The points enumerated in 3 can be expected to be discernible for a few salts, the identity of which there is no a priori way of determining.

<u>Conclusions</u> The following conclusions are drawn from this work:

1. An apparatus to give controlled cooling of a solution contained in a one liter beaker can be constructed without extensive or expensive equipment.

2. Such an apparatus can be expected to have control of the cooling rate within 0.05 degrees centigrade.

3. If such an apparatus is used for crystallization investigations of the type described in this work, two operators are required for at least part of the run if precise runs are to be consistently obtained.

4. Ammonium sulfate does not exhibit solution, supercooling tendencies in the apparatus. Solution first with a nucleus, nor where the rate of formation of new nuclei becomes zero first.

5. The points observed in 3 can be expected to be discovered for a few salts, the identity of which is no a priori way of determining.

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